LIFETIMES AND TRANSITION PROBABILITIES IN CO^+ †

G. M. Lawrence

Princeton University Observatory

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Abstract The mean lifetime of the $B\,^2\Sigma$ state of CO^+ in the levels v=0,1, 2 was determined to be 39.5 ± 4 nsec by means of the phase shift method. A modulated electron beam was used for excitation. Modulation frequencies from .54Mc to 54Mc were used to facilitate the study of cascading. A zero phase reference was obtained from the atomic lines HI, 1216A and NII, 1086A, and the effect of cascading on the phase shifts of these transitions was investigated. Values of $A_{v'v''}$ are given for some of the stronger bands of the $B\,^2\Sigma - X\,^2\Sigma$ system.

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I. INTRODUCTION

The work described here is the beginning of a continuing project aimed at determining atomic and molecular transition probabilities of astrophysical interest in the vacuum ultraviolet. As the first phase of the work a radiative lifetime experiment has been constructed and lifetime determinations made for states of CO^+.

There are only three known electronic states of CO^+, $X\ ^2\Sigma$, $A\ ^2\Pi$, and $B\ ^2\Sigma$. Lifetimes of the $A\ ^2\Pi$ vibrational levels have been found by BENNETT and DALBY[1] to range from 2.1 to 2.9 μ sec in measurements on the A - X bands (comet-tail bands). The measurements reported here deal with the transitions B - X, (first negative system) and B - A, (BALDET-JOHNSON system). Lifetime measurements have provided some of the most reliable values of absolute transition probabilities known, especially for ions and chemically unstable species. See, for example, the recent review on molecular transition probabilities by DALBY [2].

Radiative lifetime determinations have been of two types, the measurement of the time distribution of the emitted photons after excitation, and the measurement of the frequency response (phase and amplitude) to sinusoidally varying excitation. An apparatus has been assembled which uses the phase shift method of lifetime determination in which the states under study are excited by a sinusoidally modulated electron beam rather than the modulated light beam usually used. Excitation with electrons provides transitions unobtainable with photon excitation. The emitted photon flux is thus modulated at the same frequency as the electron beam but with an amplitude and phase that is dependent upon the frequency of modulation and the lifetime. Other variations of the phase shift method of radiative lifetime determination have recently been used successfully and well described by DEMTRÖDER[3] and by BREWER and co-workers[4]. The system has been built around a vacuum monochromator and can be used with a windowless detector.

The phase shift method has no fundamental advantage over a time distribution experiment as the frequency response form of the data can be obtained by a Fourier analysis of the time distribution. However, the photon source is operated continuously in the phase method and photons can be obtained at a much higher rate than in a pulsed system. The high photon rate is useful, especially for the measurement of short lifetimes where fluctuations in the photomultiplier delay time must be averaged out. The phase method uses narrow band (tuned) electronic equipment which has some advantages over the pulse equipment generally used with the time distribution type experiment. As we shall see, the effect of the instrumental frequency response is removed by the use of a reference transition. The present equipment has been constructed for use at several frequencies in order to provide measurements of widely different lifetimes and to facilitate the detection of the presence of cascading transitions from higher states than the one under study.

II. THEORY

The Phase Shift Method

We now review the time-frequency relation between excitation and radiation. If a simple upper state is excited with a short pulse (δ - function) at time $t = 0$, it emits an average photon flux proportional to $e^{-t/\tau}$, where τ is the mean lifetime of the upper state. Since the radiation has the time dependence of the upper state, we can speak unambiguously of the lifetime of the transition. If only a small fraction of the atoms or molecules are excited, the excitation-to-output relation is linear, so that the frequency response to a sinusoidal excitation $e^{i\omega t}$ is

$$(1 + i\omega\tau)^{-1} \tag{1}$$

the Fourier transform of the time response to the δ - function. This gives a

phase lag θ given by

$$\theta = \tan^{-1} \omega\tau \tag{2}$$

and an amplitude dependence of the output signal of

$$\left(1 + \omega^2\tau^2\right)^{-1/2} \tag{3}$$

We see that at an angular frequency of $\omega = 1/\tau$ (called the corner frequency), we have a phase shift of 45° and the amplitude is about to begin to fall off as $1/\omega$ with increasing frequency.

In principle, either the amplitude or phase of the modulation signal could be measured to determine the parameter τ, but because the phase dependence becomes measurable at a lower frequency than the amplitude dependence, it has been the preferred experimental quantity. The phase is also independent of pressure and electron current changes. The measurements are made with some sort of narrow band detector tuned to the modulation frequency. The statistical fluctuations in photon rate appear as white noise in the frequency domain and cause fluctuations in the instantaneous phase and amplitude.

Cascading

The major problem with the use of electrons for excitation is that higher states than the one under study may be excited and populate the desired state by cascading transitions. We can analyze the frequency response of a system with cascading by characterizing an energy state as an input-output device with a transfer function (frequency response) of $(1 + i\omega T)^{-1}$ where T is the lifetime of the state. Inputs then are excitations, either by collision or by a cascading transition and outputs are (the modulation of) radiations. As a simple model for such cascading, assume the upper state with lifetime τ is excited at a rate R by direct excitation and at a rate β R by one cascading transition from a higher state with lifetime T. We can call β the cascading fraction. Assume the higher state to be directly excited.

The frequency response of the system becomes

$$\frac{\text{Out}}{\text{Direct in}} = \frac{1}{1+i\omega\tau}\left(1+\frac{\beta}{1+i\omega T}\right).$$

The effect of such a cascading process is to add a spurious phase shift:

$$\theta_{casc} = \text{Tan}^{-1}\omega T - \text{Tan}^{-1}\,\omega T/(1+\beta) \qquad (4)$$

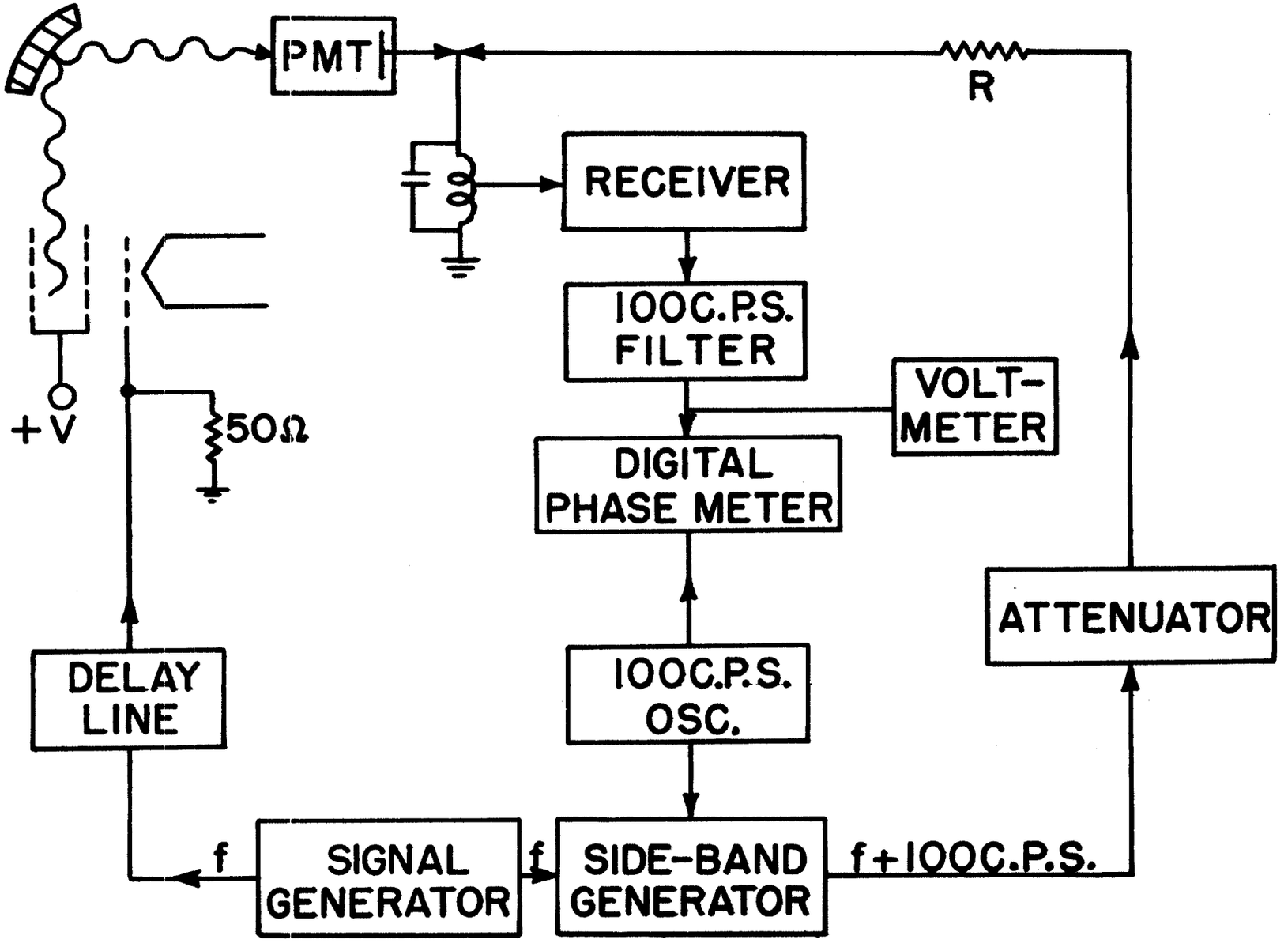
to the normal shift $\theta = \text{Tan}^{-1}(\omega\tau)$. This adds a "hump" onto the phase-frequency curve. The hump has a maximum at $\omega = \sqrt{1+\beta}/T$ and, if $\beta \ll 1$, has a maximum value of $\beta/2$.

Often, the cascading lifetimes are larger than the lifetimes of the states into which they cascade ($T > \tau$). In such cases, the cascading phase shift appears as an anomalously large phase shift at low frequencies where the normal phase shift is small. The analog of this effect in a time distribution experiment is that such cascading produces an anomalously large photon flux at large time delays.

III. EXPERIMENTAL

Apparatus

The experimental apparatus is indicated in Fig. 1. Shown in the upper left hand corner, a directly heated tungsten cathode emitted electrons for the excitation of the sample gas. The electrons were accelerated to a voltage V (20-150 volt) applied to both the second and third grids. The region between these grids was about .4 mm wide and formed the entrance slit of a Seya-Namioka vacuum monochromator. The source, monochromator and photomultiplier were all in vacuum. This system provided about 5A of spectral resolution, sufficient to isolate many individual atomic multiplets or vibrational bands of CO^+ and other molecules. The sample gas was inserted into the system through a hollow anode and had its highest pressure in the excitation region. The electron current was modulated approximately sinusoidally at a frequency


PMT
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RECEIVER
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+V
50Ω
DIGITAL
PHASE METER
ATTENUATOR
DELAY
LINE
100C.P.S.
OSC.
f
SIGNAL
GENERATOR
f
SIDE-BAND
GENERATOR
f+100C.P.S.

f by a signal applied to the first grid of the electron source. Nine fixed frequencies, spaced logarithmically from 0.54Mc to 54 Mc, as well as 45 Mc, were available for use. The photocurrent produced was thus modulated at a frequency f and contained the phase information desired. Because the anode voltage V was fed in through a terminated coaxial cable, it was possible to measure the phase stability and waveform of the electron current.

The rf path around the right hand side of Fig. 1 carried a reference signal at a frequency f + 100cps produced by the side-band generator. This signal was mixed with the photon signal to form a 100 cps beat at the output of the communications receiver. If a phase shift occurred in either of the outside rf paths shown in Fig. 1, an equal phase change was produced in this 100cps beat signal. After some filtering, the amplitude and phase of this signal were measured. Note that the voltmeter on the output of the 100 cps filter measured a signal proportional to the high frequency modulation in the photon flux. The digital phase meter was a modified time interval counter and averaged phase over an arbitrarily long period. Typically a phase measurement consisted of an average over 100 seconds with a photoelectron rate of roughly 1000/sec. Such measurements exhibited a random phase spread of approximately 2^{o}.

The following points were found to be important for the proper operation of the apparatus. The system had to be well shielded to prevent unwanted rf leakage paths, especially from source grid to the receiver input. The communications receiver had to possess enough dynamic range to carry the photon shot noise as well as the 100cps modulation. That is, it had to pass the photomultiplier pulses. The side-band generator had to have an output free from the frequency f and free from the unwanted side-band, f minus 100 cps. In practice, these unwanted signals have been kept below 2%. A calibrated delay line was used to check the accuracy of the phase measurements. At all frequencies, with the side band generator properly adjusted, the observed phase shift in the 100cps signal was equal to the phase delay in the rf path to better than 5%.

Electron Voltage

A study was made of dependence of phase reading upon electron voltage. In the range 50 to 150 volts, no measurable phase change was found with the transitions studied. Readings below 50 volts or near threshold were considered unreliable because of the relatively small signal level obtainable and because any small modulation of electron energy could produce a phase error near threshold. Because of these low-voltage effects, it was felt that any attempt to operate near threshold for the purpose of reducing cascading transitions would produce uncertain results. The results reported here were obtained using electron voltages near 100V.

Spectral Purity

It was found that it was very important to examine the spectral purity of the radiation under study. Cases were found in which the presence of unwanted spectra produced significant anomalies in the phase measurements. The measurements reported here were made with a quartz window in front of the photomultiplier when necessary to eliminate some specific 2^{nd} order interference. Some cases which were studied which were not sufficiently "clean" due to the low resolution obtainable are not reported here.

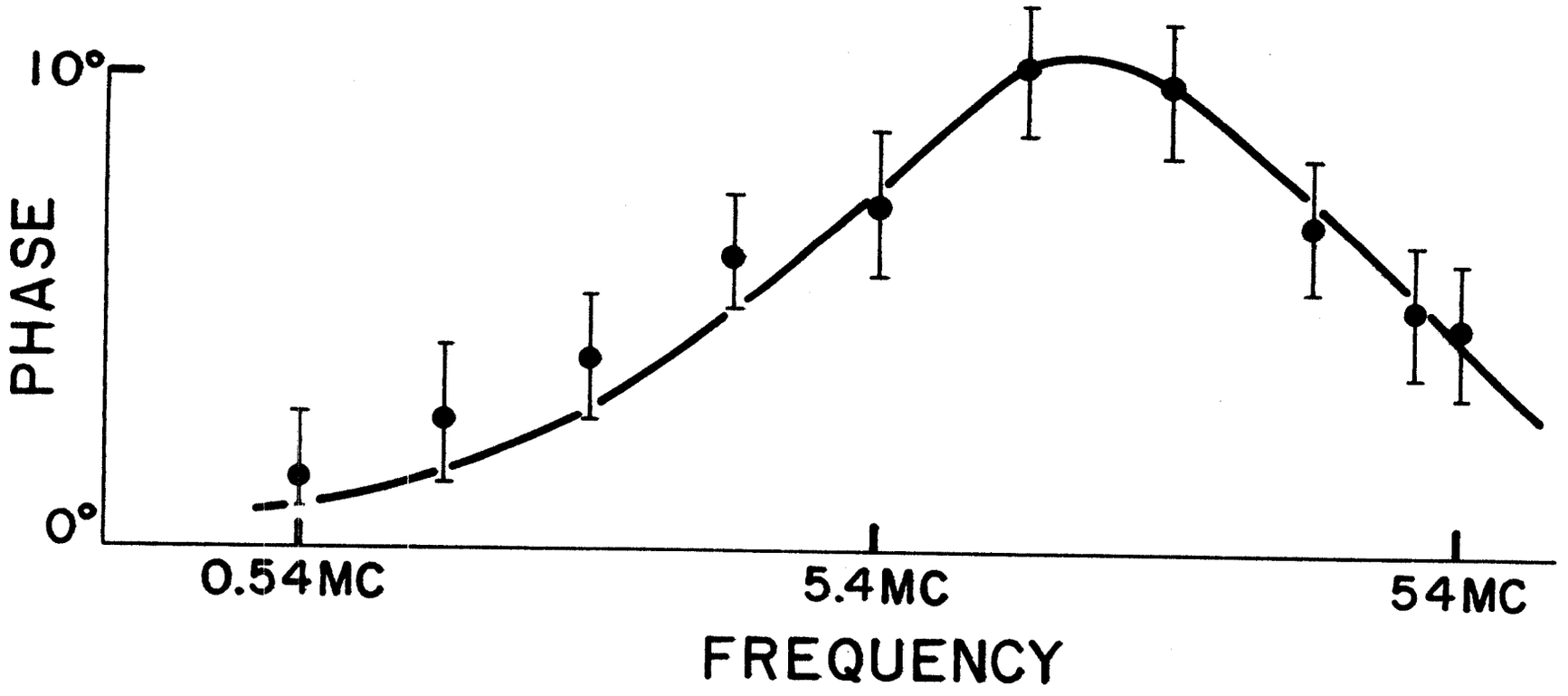
IV. RESULTS

The Zero Phase Standard

The use of the delay line for calibration determines that the system accurately measures changes in phase. However, the absolute phase reading for zero time delay in the excitation-emission process must be determined for each frequency. System delays such as the delays in the cables and the sideband generator could be determined fairly accurately but the delays associated with transit time of the electrons in the

source and in the photomultiplier are neither constant nor easily determined. The photomultiplier delay, for example, is on the order of 20 nsec. The zero phase reading at each modulation frequency is determined from measurement of the phase of a standard transition whose phase shift is known and preferably small. All of the experimental phase values were obtained as differences between phase meter readings obtained with radiation at two different wavelengths. The monochrometer wavelength drive was moved between the two wavelengths under study after each phase determination. Successive phase differences thus obtained were sometimes corrected by one or two degrees in order to compensate for the presence of a small amount of the frequency f in the output of the side-band generator.

In the measurements reported here, an atomic multiplet of N^+ at 1086A was used in obtaining a comparison standard. In the search for a suitable zero-phase reference, the relative phase shifts of several strong atomic lines were measured as a function of frequency. At the lower frequencies used for the measurements on CO^+ reported here, the N^+ 1086A transition exhibited the smallest phase shift. This was interpreted as a strong indication that it is free from cascading effects under the excitation conditions used. The line is produced by the transition $2s2p^3,\ ^3D^o - 2s^22p^2,\ ^3P$ involving the excitation of an inner electron. There is only one known, higher lying state which could populate this $^3D^o$ state by dipole radiation in a "single electron jump". A search was made with a windowless photomultiplier for the radiation of this cascading transition at 832A. Radiation near 832A was found with a strength of about 5% of that of the 1086A multiplet. However, a study of 832A strength as a function of electron voltage showed the radiation to persist down to 35 volt, whereas the threshold for the cascading state in question is 55 volt. The 832A radiation was therefore attributed to an OII resonance line excited from O_2 impurity in the N_2 sample gas. It is felt that a conservative upper limit is 2% for the strength of the cascading. A 2% cascading contribution towards the 1086A


10°
0°
PHASE
0.54MC
5.4MC
54MC
FREQUENCY

multiplet could cause a maximum error of 3% in the determination of the lifetime of the CO^+ bands.

In order to obtain a lifetime and hence a phase shift for the 1086A radiation, a comparison was made between the phase of Lyman alpha radiation excited in methane and 1086A excited in N_2. The observed phase difference as a function of frequency indicated appreciable cascading in the H atoms emitting the Lyman alpha radiation, largely due to the 3d-2p Balmer component. Use was made of the calculated lifetimes of the H states (CONDON & SHORTLEY[5]) and the experimental phase measurements to determine the cascading fraction β , and the lifetime of the 1086A line with the aid of equations (4) and (2). In Fig. 2 the phase lag of a 2.25 nsec transition (1086A) has been added to, and the phase lag of a 1.6 nsec transition (1216A) has been subtracted from the experimental phase differences. The remaining phase shift was found to fit equation (4) with a cascading fraction $\beta = 0.44$ and T = 15.6 nsec (the lifetime of the 3d state of H) as is shown in Fig. 2. To establish this fit, the lifetime $\tau = 2.25$ nsec for the 1086A radiation and the value of $\beta = 0.44$ as the cascading fraction in H were determined by an iterative process.

The sensitivity of the fit to the values of these two parameters is such that the data are consistent with $\tau = 2.25 \pm .2$ nsec and $\beta = 0.44 \pm .1$. The certain presence of some additional cascading from other H states and the possibility of a small amount of cascading into the 1086A upper state increases the uncertainty of the value of τ to perhaps ± 1 nsec. It will be noted for example, that the deviation of the points in Fig. 2 from the cascading hump at the lowest frequencies can be interpreted as being caused by the presence of cascading from longer lived states of H. Probably the next most important contribution to the cascading in this situation is the 4d-2p Balmer component which has a lifetime of 36.5 nsec.

An uncertainty of $\pm$ 1 nsec in the value of the zero reference lifetime causes

approximately ± 6% uncertainty in the determined lifetime of the CO^+ bands. Further effort is being made to determine more accurately the lifetime of the 1086A multiplet and of other atomic states.

Photon entrapment

Errors can occur in a lifetime determination if the upper state of the transition under study can be optically populated by the absorption of photons emitted by the same system. The apparent lifetime variation caused by such an entrapment of photons is dependent on the pressure of the source gas. The lifetimes reported here showed no significant dependence upon source pressure over a range of eight to one. This was expected because: 1. CO^+ was produced in small quantities by electron collisions with CO and the CO^+ ions cannot survive with appreciable density. 2. The He transition at 3889A used as a check on the method does not suffer entrapment because the triplet states of helium do not connect optically with the ground state of helium. 3. As explained earlier, the known properties of hydrogen energy levels were used in the determination of the zero phase reference of the system. The hydrogen Lyman alpha transition was studied by means of collision of electrons with CH_4, H_2, and NH_3. In these cases, the H atoms are produced in small quantities and are pumped out of the system quickly enough to prevent a significant build up of their density. Although the use of molecules as a sample gas for the study of atomic spectra prevents errors due to entrapment, it makes it difficult to predict theoretically the amount of cascading into to the 2p state of H.

Molecular Dissociation

In the studies of atomic spectra excited by collisions of 100 volt electrons with molecules, it has been assumed that the dissociation of the molecules into excited atoms takes place without delay. The molecular dissociation is expected to take place

within the period of a molecular vibration, i. e. approximately 10^{-15} sec. Comparisons of phase measurements of Lyman alpha radiation excited in H_2, CH_4, and NH_3 showed agreement at high frequencies and disagreement at low frequencies. The difference in phase shift found at low frequencies with different parent molecules was attributed to different amounts of cascading caused by differences in the production of 3d relative to 2p hydrogen atoms. The agreement at the highest frequencies indicates that the molecular dissociation process does not introduce a measurable delay.

Helium 3889A

A measurement of the lifetime of the He triplet line at 3889A was used as a partial test of the method. The large wavelength separation between this line and the 1085A reference multiplet necessitated a change in phototubes between the two wavelengths. A transition of NI at 1740A was used as a secondary phase standard which was accessible to both phototubes. The lifetime of the 3889A line obtained from the phase measurement at three appropriate frequencies is 105±5nsec. This value compares favorably with other experimental values; 115±5 and 106±5 obtained by HERON, et al. [6] and BENNETT and DALBY[7] and also with some theoretical values listed by HERON[6]. Because this lifetime is well within the frequency range of the equipment, the phase measurements were made at high enough frequency and phase shift to minimize any error caused by cascading.

CO^+

The first negative band system of CO^+, ($B\ ^2\Sigma$ - $X\ ^2\Sigma$) was excited with good intensity by the electron beam in CO at approximately one micron source pressure. The lifetime of some of these bands was determined from several phase measurements at modulation frequencies of 3.03, 5.4, and 9.6 Mc. and the application of equation (2). These frequencies gave phase shifts in the neighborhood of 45^o, the phase which gives

the most accurate lifetime determination for a given phase error. The zero phase reference was obtained from the 1086A N^+ multiplet as previously explained. The results are listed in Table I. The mean lifetimes of the v' = 0,1, 2 levels are 39.5, 39.5, and 38.8 nsec, respectively. The error estimate on the lifetime, ± 10%, includes an estimate of the systematic errors in the phase measuring system and in the zero phase reference. The differences in lifetimes of the v = 0,1,2 states were obtained from relative phase measurements between the bands. The differences are accurate to ± 1 nsec.

It is felt that there is negligable error due to cascading into the $B^2\Sigma$ states because:

1. The measured dependence of phase upon modulation frequency agrees with that expected for a cascade-free transition (Equation (1)).
2. The measured lifetimes of the v = 0,1, 2 levels agree very closely, whereas cascading would most likely contribute differently to the three levels.
3. No higher states of CO^+ have ever been observed in emmission.

In order to obtain transition probabilities for the various transitions from the $B^2\Sigma$ vibrational levels, the electronic and vibrational branching ratios must be determined. The relative strength of the B - X (first negative) band system (2000-2300A) to that of the B - A (BALDET-JOHNSON) system (3600-4200A) was approximately determined by intensity measurements of the modulated signal. Normally the B - A system is weakly excited in an electron beam in comparison to the A - X (Comet tail) system which falls in the same wavelength region. However, the long lifetime of the A - X system ($\sim$ 2.5 μ sec) meant that the signal due to this transition was greatly reduced at the modulation frequency used (5.4 Mc). This effect allowed the identification and approximate determination of the strength of the B - A band system in spite of the low spectral resolution available. The relative sensitivity of the monochromator and photomultiplier was determined between 2537A and 4200A with the aid

of an auxiliary grating, a calibrated photomultiplier and a mercury spectral lamp. The measurements yield a value of 10%, within a factor of two, for the transition probability of the B - A system compared to the B - X system.

The emission intensities of some of the stronger bands were measured in order to obtain the branching ratios from a given vibrational level of $B^2\Sigma$ to the various vibrational levels of $X^2\Sigma$. The efficiency of the monochromator-detector combination was roughly constant over the wavelength region involved (2100-2600A). The measured photocurrents were used as measures of the relative transition probabilities from a given upper state. Values of $A_{v'v''}$ obtained from these relative values are listed in Table I and are accurate to within about 5% of the total transition probability, $A_{v'}$, or 40% of the $A_{v'v''}$ value, whichever is smaller. The total transition probability is taken to be $A_{v'} = 0.9/\tau_{v'}$, thus allowing 10% of the photon flux for the B - A system. The band head wavelengths are taken from PEARSE and GAYDON [8].

The relative strengths of the bands in the system also give relative excitation cross sections for the v' = 0,1,2 levels of the $B\ ^2\Sigma$ state. The values obtained are 60, 32, and 8%, respectively which agree reasonably well with the calculated FRANCK-CONDON factors of WACKS [9] which are 68.8, 23.8, and 5.2%, respectively.

An extension of the $A_{v'v''}$ values to bands not listed in Table I can be made with the aid of calculated vibrational branching ratios, such as the FRANCK-CONDON factors published by NICHOLLS [10]. If the same is done for v', v" combinations included in Table I, by multiplying the measured $A_{v'}$ with NICHOLLS' FRANCK-CONDON factor, then agreement with the measured $A_{v'v''}$ is obtained within $0.5 \times 10^6\ sec^{-1}$.

For use with measurements of absorption intensity, electronic-vibrational oscillator strengths $f_{v'v''}$ are obtained from the relation

$$f_{v'v''} = A_{v'v''}\ 1.51\ \lambda^2\ sec/cm^2 \quad .$$

The ratio of statistical weights is unity for the B - X system. The sum of the $f_{v'v''}$ over v" = 0, 1, 2, 3, 4 with v" = 0 is 0.018± .0018 which can be used as an electronic oscillator strength for the CO^+ B - X system.

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Table I CO^+ B - X Transition Probabilities

v'	$\tau_{v'}$ (nsec)	$A_{v'}$ (10^6 Sec^{-1})	v"	$A_{v'v''}$ (10^6 Sec^{-1})	λ	$f_{v'v''}$
0	39.5±3	22.8	0	11.4	2190	.0082
			1	8.0	2300	.0064
			2	2.7	2419	.0024
			3	.45	2550	.0004
1	39.5±3	22.8	0	8.2	2112	.0055
			1	1.8	2215	.0013
			2	7.0	2325	.0057
			3	4.3	2446	.0039
			4	1.1	2578	.0011
2	38.8±4	23.2				

Figure Captions

Fig. 1. Schemantic diagram of the apparatus. Outside signal paths carry rf at 0.54 to 54 Mc. The photon path through the spectrograph is represented by wavy lines.

Fig. 2 Cascading phase shift in H 1216A excited from CH_4.
A phase dependence of 1.6 nsec for 1216A and 2.25 nsec for 1086A has been removed from the experimental phase differences. The solid curve is the calculated cascading phase (equation 4) for 3d-2p (H) with $\beta = 0.44$.

REFERENCES

1. R.G. BENNETT and F.W. DALBY, J. Chem. Phys. 32, 1111 (1960)

2. F.W. DALBY, Handbuch der Physik, vol. 27, p. 464. Springer Verlag, Berlin (1964)

3. W. DEMTRÖDER, Z. Physik 166, 42 (1962)

4. L. BREWER, C.G. JAMES, R.G. BREWER, F.E. STAFFORD, R.H. BERG and G.M. ROSENBLATT, Rev. Sci. Instr. 33, 1450 (1962)

5. E.U. CONDON Theory of Atomic Spectra, p. 136. The University Press, Cambridge (1963)

6. S. HERON, R.W.P. McWHIRTER, and E.H. RHODERICK, Proc. Roy. Soc. A234, 565 (1956)

7. R.G. BENNETT, and F.W. DALBY, J. Chem. Phys. 31, 434 (1959)

8. R.W. NICHOLLS, JQRST 2, 433 (1962)

9. M.E. WACKS, J. Chem Phys. 41, 930 (1964)

10. R.W.B. PEARSE and A.G. GAYDON, The Identification of Molecular Spectra, p. 120. Wiley, New York (1963)